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A Computational Approach to the Quantum Puzzle

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Computational physics

A quantum puzzle revisited

Computational condensed-matter physics acquires a novel compass in the search for unknown stable structures. This global phase-space search algorithm demonstrates its power in solving the complex high-pressure phases of hydrogen.

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Due to its simplicity, hydrogen is often used as a prototypical system to advance many different areas of modern physics[1]. In the field of condensed-matter physics there are a number of long-standing fundamental questions that hydrogen has refused to answer, such as will a non-metallic solid become metallic upon compression and if so will it behave as a high-temperature superconductor[2]? These fascinating questions have motivated a large number of experimental and theoretical investigations of the high-pressure nature of hydrogen. To date, pressures as high as 320 gigapascal (GPa) have been achieved using static compression methods[3], yet a low-temperature metallic phase has remained a theoretical conjecture. Instead, three distinct diatomic-molecule-based solid phases (referred to as phases I, II, and III) have been experimentally observed, though the precise atomic configurations of the latter two phases are still controversial. Elsewhere in this issue, Pickard and Needs look for novel structures in an attempt to revise the theoretical phase diagram of hydrogen[4]. In particular, their proposed structure for the highest-pressure phase (phase III) provides the first-ever satisfactory agreement with optical spectroscopy experiments.

Hydrogen represents a great challenge to researchers in high-pressure physics. Despite its apparent simplicity, both experimental and theoretical investigations of its high-pressure behaviour have proven to be exceedingly difficult. In a typical static compression experiment, a diamond anvil cell (DAC) holds a small sample of hydrogen within a gasket between two diamonds, which can be squeezed against each other. As solid hydrogen is very soft, the volume of the sample decreases by a factor of 10 by 130 GPa. Before it reaches a detector, the weak probe signal from the tiny sample will have to go through either the diamond or the gasket, which may mask the signal.

Currently, neutron scattering, the most direct and effective technique to determine the crystal structure of light nuclei, has a limited pressure range for various reasons. The highest-pressure record is only 60 GPa[5], which corresponds to phase II of deuterium. A more common direct structural measurement method, X-ray diffraction, is limited by the nature of hydrogen. X-rays primarily scatter off electrons, not nuclei. As the electronic charge distribution of hydrogen is more ellipsoidal than dumbbell shaped, it is virtually impossible to infer the orientation of hydrogen molecules based on the electron

distribution. Optical measurements such as infrared reflectivity (IR) and Raman spectroscopy have played a crucial role in identifying and characterizing the high-pressure phases of hydrogen. However, these techniques provide only indirect information on the crystal structure by measuring vibrational frequencies of hydrogen molecules, but they can distinguish crystal symmetries.

The difficulties encountered in theoretical investigations of hydrogen partly originate from the lack of direct structural information. In order to determine the most stable crystal structure, it is necessary to start with a finite set of candidate structures. Typically, the enthalpy (stability), vibrational properties or whatever quantity is measured by experiment is calculated for each candidate structure, and a comprehensive comparison then determines which structure is most consistent with the available experimental evidence. Of course, this approach is doomed to fail if the correct structure is not included among the candidates. Traditionally, researchers have relied on experience and intuition to select the set of candidate structures, which might be misleading if the correct structure is complex or unusual.

To address this problem, Pickard and Needs have developed a computational method to explore phase space effectively. Their strategy is surprisingly simple. Starting from random atomic configurations, they optimize the enthalpy given by the first-principles total energy calculation method as a function of the atomic configuration, where the shape of the simulation box is constrained such that the pressure of system is kept constant. Repeating this procedure provides a series of candidate structures, which contains the correct one if the phase space is fully explored, and if all the factors that contribute to the relative stability of the structures are accounted for accurately.

Pickard and Needs demonstrate in their work that their configuration space search was exhaustive for moderately sized computational cells, which is a significant achievement. The remaining uncertainty lies in the method used to calculate the enthalpy. Density functional theory (DFT) is known to have an excellent accuracy-per-computational-cost ratio, and therefore, is the best fit to this type of approach. Yet, it misses a few ingredients, such as the approximation of the many-body effect on electrons and the quantum statistics of nuclei[1].

In a DFT calculation, many-body effects on electrons are approximated by an effective mean-field potential derived from the local density approximation (LDA) or its improved version called GGA. The accuracy of LDA (GGA) for solid hydrogen was once questioned, as the previously most stable candidate for phase III obtained by DFT was metallic[6,7], contrary to experimental observations. By using their approach, Pickard and Needs have found a very stable insulating structure in excellent agreement with experiments on the electronic properties of hydrogen as well as the location of IR/Raman peaks and their pressure dependence. This agreement supports the validity of examining the high-pressure phases of hydrogen with DFT as well as the importance of the phase-space search algorithm.

The quantum statistics of the protons is the most challenging problem to address, particularly for phase II. As the proton (or deuteron) is a fermion, a hydrogen molecule forms a unique quantum mechanical state. The ground-state wavefunction of the protons

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[1] The non-adiabatic electron-phonon coupling is also missing important factor, however, mostly for a metallic phase; less important for an insulating phase.

in an H_2 molecule is s-wave, which is completely spherical. Upon excitation, only even numbered angular momentum states ($J = 0, 2\ldots$) are allowed[7]. The phase transition from phase I to II is interpreted as a quantum-to-quantum phase transition[8], where an orientational ordering of the angular momentum presumably takes place due to 'quantum localization'[9]. Although Pickard and Needs accounted for the quantum zero-point motion, their stable structure for phase II does not agree with experiments. Interestingly, this discrepancy may hint at the fact that fermion statistics are playing a critical role in the stabilization of phase II. More accurate but computationally expensive approaches, such as the path-integral methods where the fermion statistics of the proton can be accounted for[10], are now possible. Pickard and Needs' results could be used to choose appropriate simulation cells and starting configurations for the path-integral calculations, which could make them tractable in the not-to-distant future.

Finally, we note that the phase-space search algorithm is not limited to solid hydrogen, so it represents an exciting new tool that can be used to tackle a wide range of problems in computational condensed-matter physics.

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